Experimental study of the combustion properties of methane/hydrogen mixtures
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Chapter 6

HCN formation and destruction in atmospheric-pressure fuel-rich premixed methane/air flames
6.1 Introduction

To date, the vast majority of the methods developed to lower NO\textsubscript{x} emissions are based on decreasing the flame temperature: either through flue-gas recirculation or fuel-lean combustion. Application of these methods to obtain the lowest NO\textsubscript{x} possible ultimately leads to deteriorating flame stability. Decreasing the temperature of fuel-rich flames, which can be more stable than fuel-lean flames, is often not considered to be promising as an NO\textsubscript{x} control strategy because the key initiation reaction of the Fenimore mechanism [1]

\[ CH + N_2 = HCN + N \]  \hspace{1cm} (R6.1)

has a relatively low activation energy [2], and as such should be less sensitive to flame temperature than the Zeldovich mechanism. However, experiments performed in premixed fuel-rich natural-gas/air flames [3], showed that the measured NO mole fractions decrease with increasing upstream heat loss, suggesting that varying the flame temperature by altering the degree of burner stabilization can influence the NO production in rich flames. Recent experiments at low pressure [4] have supported these observations, and analyzed the effects of burner stabilization on Fenimore NO formation. On the other hand, it is also possible that part of the observed decrease in NO with flame temperature can be caused by the retardation of the conversion of the HCN formed in reaction (R6.1), or other fixed-nitrogen species (so-called Total Fixed Nitrogen or TFN) to NO, as suggested in [5, 6]. In this case, the “residual” TFN either will be converted to NO in the second stage of combustion or emitted into the environment with flue gases. To resolve this uncertainty, and to determine the ultimate low NO\textsubscript{x} potential of fuel-rich combustion, it is essential to measure HCN in these flames. The experimental investigations of HCN formation and destruction performed thus far have seeded flames with bound-nitrogen additives, where the reaction between CH and N\textsubscript{2} is of minor importance. HCN measurements in methane/air flames are scarce and often contradictory. For example, one study [6] reported “as \( \phi \) increases the maximum concentration of HCN increases initially, but falls again in very fuel-rich flames”, while another study [7] observed a strong increase in HCN with equivalence ratio. Moreover, Ref. [7] states that the HCN concentration is not very dependent upon the temperature, while the reported HCN
concentrations at $T = 2560$ K are almost one order of magnitude higher than those at the same equivalence ratio ($\phi = 1.20$) in Ref. [6] in the methane/air flame. Further, we are not aware of HCN measurements in which the flame temperature was varied at fixed equivalence ratio.

Although there are numerous experimental observations in fuel-rich flames (for example, Ref. [8] and references therein) showing correlations between the measured NO and CH mole fractions, as well as direct high-temperature measurements of the rate constant of reaction (R6.1) [9,10] that reasonably agree with the results of flame modeling, controversy about this reaction is not resolved [11]. Reaction (R6.1) as written is “spin-forbidden”, and to reconcile theory and experiment a near unit probability of crossing between doublet and quartet potential surfaces had to be assumed [12]. Recently, ab initio RRKM calculations have been performed for the reaction $\text{CH} + \text{N}_2 \rightarrow \text{products}$ [13,14], which showed that the reaction between CH and N$_2$ takes place mainly through the “spin-allowed” channel:

$$\text{CH} + \text{N}_2 = \text{NCN} + \text{H} , \quad \text{(R6.2)}$$

while reaction (R6.1) is not important. These calculations have been supported by NCN detection in a low-pressure CH$_4$/air flame [15], although the measurements were not quantitative. It should be pointed out that theoretical results giving (R6.2) does not contradict the experimental observations: the rate constant of the reaction (R6.1) was determined without measurement of the products, while rapid conversion of any NCN produced in (R6.2) to NO will preserve the correlation between the CH mole fraction and NO formation. The experimental determination of the concentration profiles of HCN in flames in which we expect significant Fenimore NO formation will help resolve the uncertainty as to both the primary products of CH + N$_2$ and the role of HCN as a stable intermediate in NO formation.

Towards this end we measure the axial profiles of the mole fraction of HCN in burner-stabilized rich-premixed methane/air flames at equivalence ratios $\phi = 1.3$-1.5 at different flame temperatures, similar to the method followed in Chapter 5. In these flames the HCN mole fractions are of order of a few tens of ppm. Whereas the sensitivity of the absorption method allows measuring such low concentrations, the strong background from the hot bands in the water absorption spectrum has frustrated
direct in-situ HCN measurements in flames thus far. To circumvent this problem, we follow the approach described in Chapter 4, and use microprobe sampling and wavelength modulation absorption spectroscopy with second harmonic detection, supplemented with CARS temperature measurements. As was done in Chapter 5 for acetylene, the experimental observations are compared with one-dimensional flame calculations.

6.2 Experimental

The premixed atmospheric pressure fuel-rich methane/air flames were examined using the setup and experimental methodology described in Chapter 4, and briefly summarized here. The flame temperature was varied by changing the mass flow through the McKenna Products burner and measured by broadband planar BOXCARS for nitrogen thermometry, as described elsewhere [16]. Again, the accuracy of the CARS measurements is estimated at better than 40 K [16]. The flows of all gases were measured by mass flow meters, while the equivalence ratio was determined by measuring the methane volume fraction in the unburned gas/air mixture. For calibration purposes, nitrogen doped with a known amount of HCN was flowed through the burner instead of the methane-air mixture. In the current set-up, as described in chapter 4, the accuracy of the measured HCN concentrations in the calibration gases was better than 30% at mole fractions above 3ppm. Measurements were obtained at different axial positions in the flame by moving the burner with a precision positioner relative to the CARS laser beams and sampling probe in steps of 1 mm. The sampled gas mixtures were analyzed using WMAS with detection at the second harmonic. Estimates of the sample cooling process showed that in the present setup the conversion of HCN during sampling is less than 10% for all measured flames. These estimations are supported by measurements at different suction backpressures, which showed no significant changing in the measured HCN concentration when varying pressure from 0.05 to 0.15 Bar.
6.3 Results and discussion

The measurements were performed in a set of fuel-rich flames with different equivalence ratios and mass fluxes. The flame parameters (equivalence ratios, mass fluxes and temperatures measured at 5 mm above the burner surface) are presented in Table 6.1.

<table>
<thead>
<tr>
<th>Flame</th>
<th>( \phi )</th>
<th>( \rho v ), g/cm(^2\cdot)s</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.3</td>
<td>0.007</td>
<td>1775</td>
</tr>
<tr>
<td>B</td>
<td>1.3</td>
<td>0.011</td>
<td>1855</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>0.015</td>
<td>1942</td>
</tr>
<tr>
<td>D</td>
<td>1.4</td>
<td>0.008</td>
<td>1842</td>
</tr>
<tr>
<td>E</td>
<td>1.4</td>
<td>0.01</td>
<td>1910</td>
</tr>
<tr>
<td>F</td>
<td>1.4</td>
<td>0.014</td>
<td>1950</td>
</tr>
<tr>
<td>G</td>
<td>1.5</td>
<td>0.005</td>
<td>1763</td>
</tr>
<tr>
<td>H</td>
<td>1.5</td>
<td>0.008</td>
<td>1852</td>
</tr>
</tbody>
</table>

The temperature measurements showed that all the flames studied had a domain with constant temperature extending at least 20 mm radially from the centerline, from 3 mm to 15 mm in the axial direction. Moreover, the measured temperatures in this domain were in excellent agreement with the flame calculations using GRI-Mech 3.0 [17], indicating marginal radiative heat losses in these flames.

The axial HCN profiles measured in flames with equivalence ratios \( \phi = 1.3, 1.4 \) and 1.5 are presented in figures 6.1, 6.2 and 6.3, respectively. The experimental profiles of HCN mole fraction were shifted downstream, as in done chapter 5, where the shift of ~1.3 mm was observed between acetylene concentrations profiles measured by the Raman and probe techniques. Since the equivalence ratios and mass fluxes are close to those in chapter 5, we apply the same shift (1.3 mm) to the measured HCN profiles.
Figure 6.1 Axial profiles of HCN mole fractions in methane air flames, $\varphi = 1.3$. Symbols denote probe measurements in flames A (squares), B (diamonds) and C (triangles). Lines denote flame calculations in flames A (solid), B (dashed) and C (dotted).

Figure 6.2. Axial profiles of HCN mole fractions in methane air flames, $\varphi = 1.4$. Symbols denote probe measurements in flames D (squares), E (diamonds) and F (triangles). Lines denote flame calculations in flames D (solid), E (dashed) and F (dotted).
Figure 6.3. Axial profiles of HCN mole fractions in methane air flames, $\phi = 1.5$. Symbols denote probe measurements in flames G (squares) and H (diamonds). Lines denote flame calculations in flames G (solid) and H (dashed).

As can be seen from figure 6.1-6.3, the measured HCN concentrations peak in the region of the flame front, and decrease (albeit gradually) in the post-flame zone. The maximum measured HCN mole fractions are only slightly dependent upon equivalence ratio and mass flux, and do not exceed 15 ppm in all the flames studied here. In flames with $\phi = 1.3$ and 1.4, increasing the mass flux at fixed equivalence ratio results in shifting the maxima towards the burner surface and accelerating the HCN burnout. Both effects are expected based upon the reduced degree of stabilization and the concomitant increase in flame temperature. At $\phi = 1.5$ the maximum is shifted so far downstream that the HCN burnout region is beyond the measurement domain. The observation of 5-10 ppm of “residual” HCN downstream of the flame front that is only slowly oxidized supports the conclusion drawn in earlier studies of NO formation in the burnout region of rich methane flames [5]. It is interesting to point out the strong temperature dependence of the HCN burnout. For example, the change in residence time between flames $D$ and $F$ by nearly a factor of two should lead to an increase in the HCN mole fraction at the same axial position. However, we observe a decrease in HCN mole fraction by nearly a factor of two, most likely caused by the relatively modest (~100 K) increase in the flame temperature. Also interesting is the strong shift downstream of the maximum in the HCN profiles
and the reduced oxidation rate in the post flame zone with increasing equivalence ratio at fixed flame temperature, illustrated by comparing the flames B, D and H, which have almost the same temperature (~1850 K) but increasing the equivalence ratios from $\varphi = 1.3$ to 1.5.

Large discrepancies are observed between the measured results and those calculated using the GRI-Mech 3.0 chemical mechanism. As can be seen from figures 6.1–6.3, the calculations significantly overpredict the measured HCN mole fractions for all mass fluxes at equivalence ratios $\varphi = 1.3$ and 1.4. At $\varphi = 1.5$, the calculated HCN profiles are in surprisingly good agreement with the measurements for $\rho v = 0.008 \text{ g/(cm}^2\text{s})$, while the experimental results are underpredicted for $\rho v = 0.005 \text{ g/(cm}^2\text{s})$. At the same time, GRI-Mech 3.0 predicts the qualitative trends in the burnout region reasonably well. This suggests that adjustment of the rates of the reactions that form and consume HCN in the flame front in GRI-Mech 3.0 would improve the predictions substantially.

According to the GRI-Mech 3.0 scenario, HCN is formed mainly in reaction (R6.1) between CH and N$_2$. A substantial part of the nitrogen atoms produced in this reaction will also be converted to HCN. First they react with CH$_3$ to form H$_2$CN

$$CH_3 + N = H_2CN + H \quad \text{(R6.3)}$$

and then H$_2$CN dissociates into HCN and H; here too, the HCN produced will be oxidized to NO. Oxidation of HCN in the flame front occurs mainly by

$$HCN + O = NCO + H \quad \text{(R6.4)}$$

To lower the predicted peak HCN mole fraction, either the rate of formation must be decreased or the rate of consumption increased.

To improve the agreement for the results shown above, the rate of the reaction (R6.1) must be decreased by a factor 2.5. This reaction, being the first step of the Fenimore mechanism, ultimately determines amount of NO that will be produced in fuel-rich hydrocarbon flames [1,2]; changing its rate will result in large disagreement with numerous experimental and modeling studies of the NO formation, for which there is currently good agreement [4] en references therein). Alternatively, decreasing the calculated HCN mole fraction in the flame front by varying the rate constant of the
reaction (R6.4) requires increasing its rate by more than 10 times. The rate constant of this reaction was determined both experimentally and by transition state calculations [18-20]. Very good agreement (~30%) was observed between calculations and measurements in the temperature region from 450 K up to 2400 K. Moreover, the rate constant of this reaction was used as an optimization variable for the GRI-Mech 3.0 mechanism, where it was already increased by a factor 1.45. Further increase will bring the rate constant of reaction (R6.4) far beyond the specified margins of uncertainty.

A possible explanation for the discrepancy between measured and calculated HCN concentrations can be found in considering the products of the reaction between CH and N₂ asserted in ref. [14]. The NCN formed in this reaction can be converted directly to NO in the following reactions:

\[ \text{NCN} + O = \text{CN} + \text{NO} \]  \hspace{1cm} (R6.5)

and

\[ \text{NCN} + O_2 = \text{NCO} + \text{NO} , \]  \hspace{1cm} (R6.6)

while HCN is formed in reactions

\[ \text{NCN} + H = \text{HCN} + N \]  \hspace{1cm} (R6.7)

and

\[ \text{NCN} + OH = \text{HCN} + \text{NO} . \]  \hspace{1cm} (R6.8)

Reactions (R6.5)-(R6.8) are supposed to be fast [15,21], with the result that the rate of the reaction between CH and N₂ controls NO formation. At the same time, reactions (R6.5) and (R6.6) produce NO directly while bypassing HCN formation. Unfortunately, information on NCN kinetics is very scarce. The reactions (R6.5)-(R6.8) were included in the modeling study of the NO reburning in a flow reactor [21], where their rates were estimated. It should be pointed out that the reaction (R6.6) between NCN and O₂ can be important in the fuel-rich highly stabilized flames, where oxygen is removed relatively slowly, yielding the broad flame front in which the O₂ concentrations are one to two orders larger than those of O, H and OH .
To examine the possible improvement achievable using this “NCN-route”, we perform the calculations for flame F, for which a large discrepancy between the measurements and numerical prediction is observed (figure 6.4). In these calculations, we used the same rate constant for the reaction (R6.2) as for the reaction (R6.1). Whereas this value is approximately 5 times larger than that calculated in Ref. [14], where this reaction was first proposed, it falls within the expected accuracy of the calculations. Recent modeling work [22] also suggests using the same rate constant for the reaction (R6.2) as for (R6.1), and low-pressure experiments and modeling [4] also support using this value. As can be seen from figure 6.4, using the rate constants from [21] for the reactions consuming NCN results in decreasing the maximum calculated HCN mole fraction to 29 ppm, 10 ppm less than that predicted by GRI-Mech 3.0. Putting the magnitudes of the rates of all NCN removal reactions equal to $1.0\times10^{13}\text{cm}^3/(\text{mol} \cdot \text{s})$ leads to a further 10 ppm reduction in the maximum HCN mole fraction, and brings the calculated HCN profile even closer to the measured result. Although not presented to avoid clutter in the figure, the calculations show that varying the rates of the reactions (R6.5)-(R6.8) has only a minor influence on the NO formation in these flames, this being determined by the rate of the initial nitrogen fixation reaction (R6.2).
It should be pointed out that variation of the rate constants should be performed very cautiously, remaining inside any expected uncertainty limits. A recent theoretical study [23] and experiments at room temperature [24] both yielded rates of the reaction (R6.6) between NCN and O$_2$ that are orders of magnitude lower than that from Ref. [21]. This large disparity dissuades us from trying optimizing the rate constants of the reactions (R6.5)-(R6.8) based on the results presented here. In addition, it was possible to optimize the rates to fit one experiment adequately; however, good prediction for one experiment resulted in a poorer prediction for other experiments. Further experimental and theoretical studies of NCN kinetics are needed for a better understanding of NO and HCN formation in hydrocarbon flames.
6.4 Conclusions

Axial profiles of hydrogen cyanide have been measured in laminar, atmospheric-pressure, rich-premixed, methane/air flames at equivalence ratios $\phi = 1.3$, 1.4 and 1.5. The measurements were performed by microprobe gas sampling followed by analyses using wavelength modulation absorption spectroscopy with second harmonic detection. In the richest flame under investigation ($\phi = 1.5$), very slow removal HCN is observed in the post flame zone, demonstrating “residual” HCN in the post-flame gases of fuel-rich methane/air flames. In this flame HCN concentrations of ~ 10 ppm are measured at 7 mm above the burner surface. In practical combustion systems, this HCN will most likely be oxidized to NO in a secondary combustion step. Decreasing the equivalence ratio leads to faster HCN removal in the post flame zone. When varying the flame temperature at fixed equivalence ratio no significant changes in the HCN peak concentration is observed, while the HCN removal becomes faster with increasing gas temperature.

Substantial disagreement is observed between the experimental profiles of HCN and those obtained from calculations using GRI-Mech 3.0. Changing the rates of key formation and consumption reactions showed that bringing the calculations using GRI-Mech 3.0 into agreement with the present results can be done only at the cost of unreasonable changes in the rates of these reactions. On the other hand, considering NCN as a primary product of the reaction between CH and N$_2$, based on recent theoretical studies, allows improvement in the agreement between measured and calculated HCN mole fractions. The lack of information on the rate constants of the NCN reactions at high temperatures precludes unambiguous conclusions regarding this mechanism. To provide this information we are planning to perform measurements of CH, NO HCN and NCN in low pressure flames.
Literature